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THE PREPARATION OF ALKALINE EARTH METALS FROM FLUORIDE BATHS

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THE PREPARATION OF ALKALINE EARTH METALS
FROM FLUORIDE BATHS

by

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The Preparation of Alkaline Earth Metals from Fluoride Baths.

Although at the present time little use is made of metallic calcium and magnesium, these metals might find a considerable field of usefulness, could some process for their cheap production be devised. While some alloys of calcium may find uses in the arts, it seems at present that calcium will be used to a large extent for its reducing and dehydrating qualities. Magnesium is more stable in the air, and its alloys are being used because of their lightness. It would seem that here too, the greater use lies in the utilization of its chemical properties. The synthetic reactions produced by the aid of magnesium have been carried on only in the laboratory because of the high price of the metal. If the price of these metals can be brought near to that of aluminium a market and uses would develop.

Aluminium is prepared from the oxide dissolved in fluorides, but calcium and magnesium have almost invariably been obtained from chlorides. The aluminium bath requires only a cheap oxide as ore, while the bath used for calcium and magnesium requires carefully dehydrated salts. The aluminium bath requires only occasional stir-

ring and regulation of the anodes, while calcium has to be continually watched and success can only be attained by experienced men.

The object of the present work is to try the preparation of calcium and magnesium with a bath using the oxides as raw materials. The only known solvents for these oxides which would not be decomposed before the oxides themselves are fluorides. No reference has been found in any literature to preparation of calcium from electrolysis of oxides but Tucker made some runs on magnesium oxide dissolved in fluorides.

While little information is available about the present commercial preparation of magnesium some literature has been published about laboratory experiments. All articles discuss the chloride baths. Both calcium and magnesium chlorides are very hygroscopic. The bath must be absolutely free from water to obtain successful results. F. Oettel[1] calls attention to the fact that aqueous vapors must be kept away from the magnesium bath to prevent its rapid deterioration. If water is present hydrochloric acid is liberated and magnesia precipitated in the bath. The exact reactions are difficult to determine, but the fact remains that such a bath does not produce much metal. Very pure salts are necessary and carnallite ($Mg.Cl_2$ K Cl) as found in nature is unsuitable because it contains traces

[1] Zeitschrift Electrochemie 1895 2, 394.

of sulphates. These produce explosions according to Reinhardt[1], but Oettel indicates that they oxidize the metal.

Calcium is even more difficult to prepare. Potassium chloride is not used as an addition agent because the latter alone is decomposed as observed by Matthiessen.[2] The only addition agents which have been used to lower the melting point according to the published literature are calcium fluoride and strontium chloride. Bunsen and Matthiessen indicate that from 323 to 645 amperes per square inch of cathode surface is a suitable current density for a commercial process.

The general object of these experiments was to determine whether a bath made up of fluor spar and lime with other addition agents would be a commercial possibility. The materials used were of commercial purity, not of the chemically pure grade.

Potassium as before mentioned can not be used in a chloride bath for preparing calcium. It is extremely unlikely that it can be used in a fluoride bath. No chlorides or less stable compounds can be added without being decomposed. The only possible solvents remaining are barium and strontium fluorides. In the bath, barium fluoride,

1. Dingl 1855, 174, 141.
2. Liebigs Ann. 1855, Vol. 43, page 277.

being dense, would help to make the metal rise.

Experimental work was begun by determining the fusibility of these fluorides mixed with fluor spar and quicklime. Calcium and barium fluoride were first tried in varying proportions. A granular carbon resistance furnace was used for heating a graphite crucible which contained the bath. A cobalt-nichrome thermocouple was used to determine the temperatures. It was found that the cooling curve showed no appreciable change at the freezing point so that the rigidity of the mass had to be noted directly.

Equimolecular quantities of calcium and barium fluoride were first tried because the thermocouple would not stand the high temperature of the pure molten fluor spar. The mass melted at 974° centegrade. Calcium fluoride was added to the mass. The melting point rose only slightly, but the pastiness of the material became more marked above the melting point.

Calcium fluoride	barium fluoride	M.P.° C.
39 grams	87 grams	974°
59 grams	87 grams	977°

This pastiness before freezing is probably due to a part of the material becoming solid before the rest. It would indicate that the eutectic mixture contained more barium. Consequently experiments were tried adding more barium fluoride.

Calcium fluoride	barium fluoride	
39 grams	78 grams	975°
39 "	96 "	981°
39 "	174 "	981°

It was decided that the bath should contain as much calcium as possible without destroying the fluidity. It follows from these data that the lowest melting mixture is in the neighborhood of molecular proportions. Since the addition of lime would probably react with some barium fluoride forming calcium fluoride and barium oxides, it was decided that a slight excess of barium fluoride would be advantageous. The next experiments were made on mixtures of lime with the fluorides of barium and calcium.

calcium fluorides	barium fluoride,	calcium oxide	M.P.
39 grams	105 grams	------	982°
39 "	105 "	2.8	963°
39 "	105 "	5.6	965°
39 "	105 "	10.2	962°
39 "	105 "	21.2	965°

It was found as shown above that the first addition of two per cent of the bath produced a lowering in freezing point of about 20°C. The remaining 12% produced no noticeable change.

Strontium fluoride was next prepared by the double decomposition of strontium chloride with potassium fluoride. The precipitate was very difficult to wash by suction, and washing by decantation could only be used. Melting point determinations were made by adding this to the bath containing barium fluoride and calcium fluoride and oxide. The

results are not very reliable because the mass was so pasty that it could hardly be said to have a melting point.

		M.P.
105 grams	barium fluoride	
40 "	calcium fluoride	
5 "	calcium oxide	962°
with 2 grams	strontium fluoride	950° (pasty)
" 7 "	" "	965° "
" 18 "	" "	960° "
" 38 "	" "	982° "

A mixture of lime with calcium and barium fluorides was fused in the usual way. Strontium fluoride was added. The first two grams produced a slight lowering in melting point (from 962° to 950°) but made the mass more pasty. The addition of more raised the melting point and made the mass very pasty. 38 grams was added in all to the original mixture. It was noticed that the mass formed a scum and boiled very vigorously on heating. This would indicate the presence of carbonates. A better way to prepare the salt would be by the use of hydrofluoric acid.

Strontium salts are much more easily decomposed than barium salts; because of this and the fact that they did not lower the melting point materially, no strontium was used in the bath. There should be sufficient oxide in the bath so that oxygen will be liberated at the anode.

It was decided that in all runs the anode and cathode should be as far apart as possible to prevent carbon monoxide from migrating from the anode to the cathode and uniting with it. A graphite lined box could very well be

used as an anode in melting up the liquid, but since the gases might rise through the electrolyte from the bottom it was decided best to have a separate anode while attempting to produce metal.

EXPERIMENT I.

A bath was made of 55 parts barium fluoride, 25 parts calcium fluoride and 20 parts lime. A cast iron box, (7" x 7" x 7",) lined with graphite plates was used as a container and as anode while the bath was being melted. A round piece of iron five-eighths of an inch in diameter was used as a cathode throughout the run. This cathode was fastened in an adjustable holder which could be easily raised or lowered while the current was flowing. An additional electrode consisting of an arc light carbon in a holder was used to start the fusion of the bath. The whole bath was melted down in two hours using a current of 300 - 400 amperes. Then a carbon anode one-half inch in diameter was inserted at the corner of the bath opposite the cathode. The box was disconnected and 100 amperes passed through the new anode. The bath cooled off slightly, forming a crust as was desired. After the anode had been used for a few minutes, the "anode effect" appeared. This has been noted in many other fused electrolytes. Its appearance at this run was very characteristic. About every minute or half

minute a mass of flame, appearing as though it were some metal, rose to the surface, seemed to cling to the anode, and then the flaming mass would run off to the side. This phenomenon produced the impression that metal was coming from the electrode. A volt meter, however, showed that the carbon was really the anode. The current dropped to one-half the previous value and the voltage rose from 30 to 70 volts as soon as this effect was noticed.

This heating at the anode seems to be due to a film of gas produced by an excessive current density. It was therefore decided to use a larger anode in the succeeding experiments.

EXPERIMENT II.

The bath had been allowed to freeze in the box with the cathode. The mass was remelted by the aid of an additional electrode in series with a water rheostat. An arc was struck from the cathode to this electrode and within fifteen minutes the side of the box which had been connected as anode was carrying current. The bath was heated by passing 300 amperes at 30 volts for an hour and a half. A round carbon anode one and a quarter inches in diameter was inserted in the corner opposite the cathode. A large current (200-300 amperes) could be passed without producing the anode effect. It was noticed that the bath was not molten around the cathode. The bath was stirred with a

carbon rod to bring the unmelted portions into solution. It was found that the mass was very solid as if it were all metallic iron and it could not be made to melt. The cathode was raised out of the bath and the current turned off.

It was found that a heavy deposit three inches in diameter was firmly attached to the cathode. After cooling the mass it was broken off with a hammer. It was very tough and had the odor of calcium carbide. Fresh pieces thrown into water acted like a poor grade of carbide. The mass was also found to conduct electricity as well as calcium carbide. Some pieces were preserved in a bottle and later tested.

The pieces were broken into small lumps and placed in a small flask. A thistle tube was inserted to add water and acid. All the escaping gas had to pass through caustic and into an ammonical silver solution. The material showed very little action with water and produced heat when hydrochloric acid was added. Very little gas was evolved and no explosive precipitate was formed with the silver solution. The pieces were disintegrated and much carbon was left as a black powder. Similar pieces when left in the air for two weeks showed disintegration and a white residue. This would indicate that the carbon was volatile. It is not necessary that the entire mass should have the same composition, but it seems fairly certain that carbon

is one of the essential constituents of this cathode deposit. In any event, this deposit conducts electricity as a conductor of the first class and tends to fill up the bath with infusible material.

The presence of free carbon or carbides at the cathode can be satisfactorily explained. It is known that magnesium will reduce carbon monoxide and carbon dioxide to carbon and magnesium oxide. Calcium acts as a more vigorous reducing agent than magnesium.

It is also known that graphite or carbon crucibles are unsuitable for melting calcium because a combination takes place. We have all the conditions necessary for the formation of calcium carbide or other similar substances if the bath contains carbonates or if carbon monoxide is dissolved around the anode. It is possible that the carbon is uncombined or that a different carbide or fluoro carbide is formed. This would be difficult to determine because the entire cathode deposit contains so much bath, and does not contain crystals visible to the eye.

The only possible means to prevent the formation of this deposit are: a bath entirely free from carbon dioxide and a diaphragm between anode and cathode. No anode besides carbon or graphite has ever been found suitable for a fluoride bath. All metals that are commercially available would be attached and any oxide, as magnetic oxide of

iron would be at once dissolved.

EXPERIMENT III.

Extra fresh quicklime was used in the preparation of this bath. The proportions were the same as before and the anode, cathode and the container were the same. It was found that the bath could be started by producing an arc from the iron cathode to the graphite in the box. Bath was thrown in at once and melted very quickly. Practically no iron from the cathode was lost in this stage. The same current was used for melting (300 amperes) for one and a half hours. It was found that not so much of the cathode deposit had formed. Then the cathode was raised so as to increase the current density an arcing effect with a brilliant white flame was produced which melted off the cathode deposit. After melting off the cathode deposit several times, it was found that the cathode became too short to reach the electrolyte, and the current was consequently turned off.

During this run the first signs that a metal was being burned at the cathode were noticed. This appeared only when the cathode density was so high (300 amperes per square inch), the appearance of an arc was produced. In this connection Bunsen and Matthieson have recommended current densities from 300 to 600 amperes per square inch for chloride

baths.

The cooling effect of a bar will depend on its cross section. For this reason a cathode of larger cross section was used.

EXPERIMENT IV.

The same bath was used as before. A round iron cathode one inch in diameter was used. The same box before mentioned was used as a container and the same anode. The bath was melted with the same current as before. This was lowered to 200 amperes and the cathode raised out of the liquid until just the end touched. A two inch iron pipe was lowered around the cathode to catch any metal which might form. The upper part was closed with asbestos. In a short time a hole was burned in the side of the pipe.

When the bath was examined, it was found that the cathode deposit had formed. Since this conducts electricity, trouble would occur wherever it touched the pipe. It was decided to use a larger pipe for subsequent runs. Also the pipe had become immersed too deeply in the bath. This caused it to act as an intermediate electrode. The bath inside of the pipe seemed to contain much iron.

EXPERIMENT V.

This was similar to the previous experiment except that a two and one-half inch pipe was placed around the ca-

thode. The pipe lasted longer but no metal or bath containing finely divided metal was found.

It is well known that at lower temperatures the metal does not redissolve so readily in the bath. The very high temperatures resulting from the high current densities made the process unsuccessful. The cathode deposit was invariably formed, It would be expected that if the carbon found in it was due to carbonates in the lime, that after this bath had been used a long time it would cease to form. It seems more probable that carbon monoxide dissolves in the bath and thus comes to the cathode. If this is so, the deposit could be stopped most effectively by a diaphragm.

EXPERIMENT VI.

A perforated piece of sheet iron one-sixteenth of an inch in thickness and having holes of about the same diameter was placed in the bath from one corner of the box to the opposite one. The box and electrodes were the same as in experiment II. This iron plate was used for about ten minutes when it was found that the center was entirely corroded.

The only sort of a diaphram suitable must be a non-conductor. No fire clay materials or porcelain plates would be suitable as they would be dissolved by the fluorides-

The only possible permanent diaphragm may be produced by using the bath itself kept in a frozen condition by a

cooling coil. No indications were found that metal had been produced, so no further experiments were made along this line.

The next experiment was made with the hope that a water cooled cathode would permit a high current density without allowing the bath to become so hot. This has been found very successful for electrolysis of the calcium chloride.

EXPERIMENT VII.

A one inch pipe was fitted with a nipple and a plug. A smaller pipe was placed inside for carrying the water down to the bottom. A reducing tee was used to let the water in and out.

The box was used as cathode and a carbon of the usual size placed in the former cathode holder. This method was found a very poor method for trying to melt the bath. Only that portion within half an inch of the anode melted and this was very hot.

This shows that much heat is generated around the anode and less at the cathode. When the anode consisted of the whole box the heat was distributed, but in this way all the heat was generated at one spot and the rest would freeze again if melted by stirring.

EXPERIMENT VIII.

This experiment was identical with the former except that the box was used as anode and an iron cathode inserted.

The melting of the bath was easily accomplished as in the earlier experiments. Water was allowed to pass through the cathode and it was lowered into the bath two inches. The iron rod was raised and the current lowered to about 200 amperes. At this current a crust formed.

The water-cooled cathode was not found of special advantage. The cathode deposit was found present and the effect of the cooling water would not be of much use when there was a thick layer of conducting material around it.

From these experiments it would seem that calcium could not be prepared from a fluoride bath. The principal difficulty is that the calcium is effected by the presence of carbon, which it the only suitable anode material. Since very little gas was evolved at the anodes during any of these experiments it seems that it dissolves in the molten bath.

Magnesium does not so readily form carbides. Investigators have suggested the addition of barium salts to chloride baths to increase the density and thus bring the magnesium to the surface.

EXPERIMENT IX.

A bath was made up of approximately two parts barium fluoride and one part magnesium fluoride.

This was melted in a cast iron unlined box twelve inches long and six inches deep and wide. The same anode

and cathode were used as before. The box was filled two-thirds full of bath. An arc was struck from an electric light carbon to the cathode and a little of the bath melted in this way. The carbon was placed in the molten bath and slowly moved over toward the permanent anode. At 100 amperes the anode effect was very much more violent than it had been during any experiments on the calcium bath. In one hour the bath all around the anode was well melted while the rest of the bath had a very thick crust, so thick, indeed, that there was no sign on the surface that electrolysis was going on. Occasionally a gas burning with a yellow flame appeared at the cathode. The flames produced a white deposit on the objects above them but the flame itself formed a black deposit on cold objects. The current was reduced to fifty and finally to twenty amperes without overcoming the anode effect. The allowable current per inch of anode surface would be about 7 amperes per square inch.

The solidified bath, on being removed from the box, showed that some sort of metal had been formed around the cathode, The entire bath had become black and parts of it showed violent effervescence and produced sparks when treated with water. Substances which had a metallic appearance when freshly broken were noticed to lose their luster in the air very quickly.

EXPERIMENT X.

The same box used in experiment IX was used as a cathode and five carbon electrodes of the usual size ($1\frac{1}{4}$") were used as anodes. An arc was formed between one carbon and the box and bath was then fed in around the carbon. The others were started with the help of an arc light carbon. This was inserted in the bath and pressed against an anode thus making an additional movable electrode. A current averaging 120 amperes was passed during the two hours' run. Globules of magnesium were found distributed like shot throughout the lower layer of the bath. This fact would indicate that the black layer of bath near the cathode conducts electricity as a first class conductor. Tests were made on pieces taken from the bath and it was found to be a conductor at room temperatures. This deposit had an appearance similar to that formed by calcium bath except that it was not so dense nor so tough. It seemed probable that this deposit contained barium carbide. No metal losing its luster in the atmosphere was found. This may be attributed to the fact that in this experiment a large cathode was used while in the previous experiments only the small cathode surface of the 5/8" rod was employed. The higher current density would tend to plate out a small amount of barium while at the lower current density only magnesium

would be expected.

The trouble here was that there was no definite cathode because the cathode deposit conducts the bath. It was determined to try a bath free from all carbide forming elements.

EXPERIMENT XI.

In place of barium fluoride to lower the melting point, potassium fluoride was added to the magnesium fluoride. The magnesium salt was prepared by neutralizing hydrofluoric acid with pulverized magnesium oxide containing a little carbonate.

The oxide was added in the dry form until no more carbon dioxide was evolved. The weight of the dried salt so formed was 25% more than the theoretical amount which could be formed from the acid. Potassium fluoride was dried over a gas flame in an iron dish. It was found so solid that a cold chisel had to be used to remove it from the dish. The two were mixed, about four parts of magnesium fluoride with one of potassium fluoride. The bath was melted with the same apparatus as before, except that three anodes were used. One hundred amperes were passed for three hours. When the bath was all melted and the anodes immersed to a depth of two inches no anode effect was noticed. During this experiment the yellow flames were not noticed continually. Several times short circuits occurred. After

this pieces of magnesium could be seen to produce little explosions in burning.

After cooling over night the bath was taken out of the iron box. It was found that a soft metal, stable in the air, had plated the box in various places. This was not tested as the globules were, because it could not be separated from the iron without a cold chisel and a cold chisel would remove the iron also. The bath did not show any formation of a black deposit but was homogeneous throughout.

EXPERIMENT XII.

A run on a larger scale was attempted. Hydrofluoric acid was neutralized half way by potash and magnesium oxide was added till no more action was noticed. The salt formed was not hygroscopic.

A carbon lined box (8" x 8" x 16" inside) formerly used for the preparation of aluminium was used. It was found that the bath could not be melted at all. Addition agents as caustic potash, ammonium fluoride, and finally barium fluoride were added, producing only a pasty mass. A current of 300 to 400 amperes was used in the first six hours to heat the whole bath and after that 150 amperes was passed.

It is remarkable that the voltage did not vary directly with the current. The resistance adjusted itself in time. The average current passed for 8 hours was 231 am-

peres with an average pressure of 22 volts. The maximum voltage ever used was 30 volts.

The yield of metal was no better than any previous experiments using barium. It shows, however, that even a small amount of barium salts is sufficient to produce considerable cathode deposits and prevent the globules of magnesium from adhering together. No current efficiency could be determined because no large pieces were found.

The peculiar result of this last experiment is that a bath prepared from the same materials containing less potassium chloride melted readily, while the bath containing more refused to melt at all. A variation in the quantity of magnesia might possibly account for this trouble. It is also possible that the compound $Mg F_2. 2KF$ does not melt readily. Experiments showing the effects of various amounts of potassium fluoride and magnesium fluoride would be very interesting. Experiments determining whether sodium is formed at the cathode before magnesium separates out should be tried.

While magnesium may be produced from oxide ores by using fluoride baths, it still remains doubtful whether there will be sufficient current efficiency to make the process commercial. It is very possible that carbon monoxide formed at the anode should dissolve in the bath and migrate to the cathode here oxidizing some of the magne-

sium. Also the bath does not melt at as low a temperature as does the chloride bath. The power of the bath to redissolve the metal has always been found greater at higher temperatures than at lower ones. Experiments must be tried on readily fusible baths.

In conclusion, the most important result of this thesis is that calcium and barium salts are to be avoided with fluoride baths. Also, it has been found possible to obtain magnesium by a process using the oxide as an ore, but the commercial superiority has not been proven as yet.

Approved by Oliver P. Watts

Professor.

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